

INDUCED RADIOACTIVITY IN EUROPIUM

By

KASIMIR FAJANS AND DAVID W. STEWART

INDUCED RADIOACTIVITY IN STRONTIUM AND YTTRIUM; NUCLEAR ISOMERS IN STRONTIUM

By

DAVID W. STEWART

PART I

INDUCED RADIOACTIVITY IN EUROPIUM

By

KASIMIR FAJANS AND DAVID W. STEWART

PART II

INDUCED RADIOACTIVITY IN STRONTIUM AND
YTTRIUM; NUCLEAR ISOMERS IN STRONTIUM

By

DAVID W. STEWART

FROM THE DISSERTATION OF
DAVID WYLIE STEWART
SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE
UNIVERSITY OF MICHIGAN

1939



Induced Radioactivity in Europium

KASIMIR FAJANS AND DAVID W. STEWART*

Departments of Chemistry and Physics, University of Michigan, Ann Arbor, Michigan

(Received August 16, 1939)

Europium oxide has been bombarded with slow neutrons from the cyclotron for periods ranging up to about five months, and with 7-Mev deuterons for much shorter lengths of time. By reduction of the europium to its bivalent state, it has been possible to separate this element from neighboring members of the rare earth group. By slow neutron activation, two periods of induced radioactivity have been produced in europium; one, with a half-life of 9.4 ± 0.2 hours, is assigned to Eu^{152} , in accordance with the results of other investigators. This isotope probably decays both by the emission of negative electrons and by the capture of K electrons. The beta-spectrum, as measured in the cloud chamber, has an upper limit of 1.83 Mev. The second period, produced only after long

exposure, has not decayed appreciably in six months. It has been assigned to Eu^{154} . Preliminary studies indicate that K -electron capture may also take place in the decay of this isotope. The upper limit of the beta-spectrum has been found to be 1.0 ± 0.1 Mev. By relatively short deuteron bombardments, the 9-hour period has also been produced, and in addition two new periods of 12 ± 4 minutes and 105 ± 5 minutes have been obtained. These could not be separated from the 9-hour activity by chemical methods, which indicates that they are due also to isotopes of europium, probably to isomeric forms of Eu^{152} and Eu^{154} , not produced appreciably by slow neutron activation.

INTRODUCTION

RADIOACTIVITY induced in europium by the action of neutrons had previously been studied by Sugden,¹ Marsh and Sugden,² Hevesy and Levi,³ and Pool and Quill.⁴ Europium, like cerium, differs from other members of the rare earth group in that it may be separated from neighboring elements by a single chemical operation with satisfactory completeness, and for this reason it has been feasible to study more carefully the radioactivity induced in it by deuteron as well as by neutron bombardments. The stable isotopes of europium and adjacent elements are shown in Fig. 1, where the figures refer to percent abundance.

Previous investigators had found in europium a negative-active period of 9.2-hour half-life. On the basis of experiments with fast neutrons, this activity has been shown by Pool and Quill⁴ to be due to Eu^{152} . These same experimenters have reported a period of 27 hours, which they observed only after fast neutron activation, and have assigned this to Eu^{150} , which is reported to

emit positrons. In the present study, slow neutrons were used to extend the previously known results, and deuterons were also used to search for new radioactive isotopes. Cloud-chamber studies were made of the radiations from certain of the artificially produced radioelements.

MATERIALS AND APPARATUS USED

Europium oxide was obtained from Professor H. N. McCoy, who made the original purification. To remove traces of the lighter elements, such as sodium, the europium was twice precipitated from acid solution by oxalic acid, with ignition each time to the oxide. An examination of the arc spectrum of the material with a Littrow quartz spectrograph failed to reveal impurities of other rare earths, or of any of the common elements.

A further question as to the purity of the material was raised after electroscopic measurements on 0.5-gram samples showed that natural

* Present address, Department of Chemistry, Columbia University, New York.

¹ S. Sugden, *Nature* **135**, 469 (1935).

² J. K. Marsh and S. Sugden, *Nature* **136**, 102-3 (1935).

³ G. v. Hevesy and H. Levi, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.* **14**, No. 5 (1936); also *Nature* **136**, 103 (1935), **137**, 185 (1936).

⁴ M. L. Pool and L. L. Quill, *Phys. Rev.* **53**, 437-46 (1938).

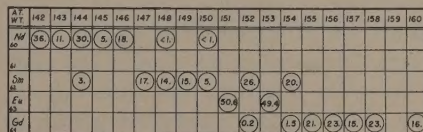


FIG. 1. Stable isotopes with their relative abundance.

radioactivity, with an intensity of the order of magnitude of the natural leak of the measuring instrument, was present before bombardment. Tests on larger samples of the europium oxide resulted in the identification of traces of mesothorium, radiothorium, thoron, and subsequent members of the natural thorium series, and a method was devised to remove all detectable natural radioactivity. The method of Kaufman⁵ was used, in which a small amount of europium iodate was precipitated to act as a carrier for the less soluble thorium iodate. This was followed by the precipitation in the solution of barium sulfate to act as a carrier of radium and lead isotopes. By repeating this process, and finally reprecipitating the europium, a quantity of material was prepared in which no natural activity of any kind could be detected. This europium oxide was then used for all further experiments.

Deuterons were accelerated in the cyclotron, where a beam of from 10 to 20 microamperes at 7 Mev was usually available for direct bombardments. For the production of neutrons, beryllium was bombarded with larger currents of deuterons at somewhat lower energy.

Measurements of the radioactivity were made with a Lauritsen type electroscope. The sensitivity of this instrument was frequently checked with a standard uranium oxide source, and all readings were reduced to a constant sensitivity.

The sign of the particles emitted and the energy of beta-rays were measured in a cloud chamber 12 inches in diameter, in a magnetic field uniform to about ± 0.5 percent over the volume of the chamber. The chamber was filled with hydrogen, and alcohol and water were used as condensable vapor.

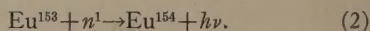
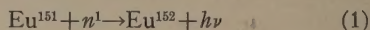
SLOW NEUTRON ACTIVATION

Europium oxide was surrounded by paraffin and exposed to neutrons from the cyclotron. The strongest activation was obtained in an exposure which lasted from August, 1938, to January, 1939, during which time the cyclotron was operating intermittently with varying efficiency. This sample showed a strong initial

decay in the previously known period, here observed to be 9.4 ± 0.2 hours, and then further decay in an extremely long period. In six months following bombardment, the intensity has remained constant within the experimental error of about one percent. The sample now has an activity about sixty times as great as the background of the electroscope, and further measurements of the decay are being made.

To make certain that the long period activity was not due to remaining traces of the naturally-active contaminant, previously detected and removed, the sample, following bombardment, was dissolved in nitric acid and barium sulfate was precipitated in the solution. The sulfate precipitate carried with it less than one percent of the long period activity, whereas the same treatment had removed almost all of the beta-activity of the natural contaminant. The bombarded sample was also much more active than could be explained on the basis of a remaining trace of radioactive impurity. It may thus be concluded that both periods observed are due to isotopes of europium produced by the capture of slow neutrons. No periods shorter than the one of 9.4 hours could be detected, even in samples bombarded for much shorter intervals of time and measured within five minutes after bombardment.

If, following the work of Pool and Quill,⁴ the 9-hour activity is assigned to Eu^{152} , the long period most probably belongs to Eu^{154} . The two observed slow neutron reactions are thus:



The observation of a new, long-lived radioactive isotope, with its assignment to Eu^{154} , explains the results of Hevesy and Levi³ and others who have found an abnormally high absorption in europium for slow neutrons without detecting the long period.

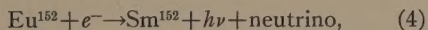
Radiations connected with both periods have been examined. The energy spectrum of the 9-hour beta-rays was measured in the cloud chamber in a field of 334 gauss. From a distribution of 840 tracks, the observed upper limit was found to be 1.83 ± 0.05 Mev. This is in agreement with the value of 2.0 Mev found by Hevesy and

⁵ L. Kaufman, J. App. Chem. (U. S. S. R.) 9, 918-24 (1936).

Levi from absorption measurements, but does not agree as well with the value of 2.6 ± 0.4 Mev reported by Naidu and Siday.⁶ Subsequent to the present work, the authors supplied a sample of the material to Mr. A. W. Tyler, who has investigated the radiations in a magnetic spectrometer. His value of 1.885 ± 0.012 Mev for the upper limit of the electron spectrum⁷ is in good agreement with that reported here.

Absorption experiments on the 9-hour radiation showed that gamma-rays of at least two different energies accompanied the beta-rays. From absorption in aluminum, the softer component was found to have an energy of about 50 kev. If Eu^{152} decayed to Sm^{152} by the capture of a K electron as well as to Gd^{152} by the emission of a beta-particle, the K radiation expected from samarium would have approximately the observed energy. Samples of europium were furnished to Dr. J. R. Richardson, who made a study of the gamma-radiation in the cloud chamber. His results⁸ show gamma-ray lines at 45 kev, 0.31 Mev, and 0.9 Mev, and he has concluded that the K -electron capture is a probable process in the decay. Tyler⁷ has also found these gamma-ray lines, and in addition three other lines, some of which are internally converted, and which may account in part for the presence of K radiation. It is not yet clear whether the higher energy gamma-rays are associated with an electron capture or with the beta-decay process.

The two decay mechanisms, represented by the equations



are in accord with the behavior predicted by Sizoo⁹ for three isobaric nuclei of consecutive atomic number, the first and third of which are stable, and the second beta-radioactive.

Radiations from the long period of Eu^{154} have not been studied so completely. The particles emitted were found to be negative electrons, and gamma-radiation was also found to be

present. Absorption measurements in aluminum showed that the beta-rays have an upper limit of 1.0 ± 0.1 Mev, and this value has been confirmed by preliminary cloud-chamber measurements. The energy of the gamma-radiation has not been measured because of the low intensity available. Analogous considerations to those above suggest that Eu^{154} may also decay both by the emission of beta-particles and by the capture of K electrons. In this case also, the two product nuclei, Gd^{154} and Sm^{154} , are stable isotopes.

DEUTERON ACTIVATION

Europium oxide was bombarded with deuterons for periods ranging in length up to about five hours. With the usual currents, this represented a maximum of less than 100 micro-ampere-hours, at from 6 to 7 Mev.

Following bombardment, europium was separated chemically from other elements which might be formed. This was done by passing a solution of europium chloride through a Jones reductor, in which zinc and dilute acid reduced the trivalent europium to its bivalent form, from which it could be precipitated as EuSO_4 , which is insoluble. The reduction process is a specific separation of europium from almost all other rare earth elements, since other members of the group can be reduced only with much greater difficulty, if at all. The nature of the separation and the conditions under which it is carried out have been described by McCoy.¹⁰ Lanthanum chloride was added before reduction

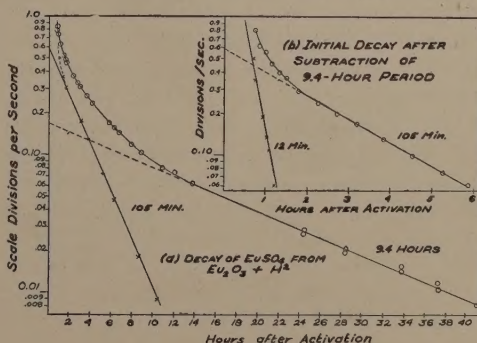


FIG. 2. Decay of Eu from $\text{Eu} + \text{H}_2$.

⁶ R. Naidu and R. E. Siday, Proc. Phys. Soc. (London) 48, 332-36 (1936).

⁷ A. W. Tyler, Phys. Rev. 56, 125-30 (1939).

⁸ J. R. Richardson, Phys. Rev. 55, 609-14 (1939).

⁹ G. J. Sizoo, Physica 4, 467-72 (1937).

¹⁰ H. N. McCoy, J. Am. Chem. Soc. 58, 1577-80, and 2279-81 (1936); 59, 1131-2 (1937).

to serve as a carrier for the other rare earths, and was reprecipitated as the trivalent oxalate by the addition of oxalic acid, after the removal of the europous sulfate.

The decay of a sample of EuSO_4 from Eu_2O_3 activated by deuterons and separated in this way is shown in Fig. 2. The analysis shows three periods of decay: 9.4 ± 0.2 hours, 105 ± 5 minutes, and 12 ± 4 minutes. The decay of the unreduced fraction, which should contain any other rare earths produced by transmutation reactions, showed only these same three periods and in much lower intensity, probably due to small amounts of europium not completely reduced by the zinc.

To investigate whether the periods observed in the EuSO_4 were all due to isotopes of europium, the ratio of their initial intensities, corrected for an infinitely long bombardment time, was calculated and compared with the ratio extrapolated from the decay of a sample of europium oxide which was not treated chemically after bombardment. The corrected intensity ratio for the periods 9-hour : 105-minute : 12-minute, was found to be 1 : 1.5 : 10, within the limits of accuracy of the analysis, for both samples. Since the 9-hour period is known to be due to Eu^{152} , from work with neutrons, and since there was no detectable fractionation of the other two activities in the chemical separation, it seems most likely that all three are due to isotopes of europium. In addition, it may be

noted that most isotopes in Gd or Sm, to which usual (H^2, n) and (H^2, α) processes from europium might lead, are stable or have known radioactive periods quite different from any of those observed here. This is in accord with the view that the periods observed are due to isotopes of europium.

Deuteron bombardments prolonged enough to produce the long period of Eu^{154} could not conveniently be performed, but the 9.4-hour period from deuteron activation was undoubtedly the same as that assigned to Eu^{152} . The two shorter lived isotopes produced by deuterons were not observed after neutron activation. Chemical evidence, which indicates that they are isotopic with the 9-hour radio-europium, suggests that they may be due to isomeric forms of Eu^{152} and Eu^{154} which, as shown, are produced much more easily by deuterons than by neutrons. It has not been possible to decide to which isotope each period belongs.

We are indebted to Professor H. N. McCoy for the europium oxide used, and to Professor J. M. Cork, Dr. B. R. Curtis, and to other members of the Department of Physics for their interest and cooperation in making the bombardments and the cloud-chamber studies. Mr. Norman Bauer and Mr. William H. Sullivan assisted in purifying the europium and in making cloud-chamber measurements. The investigation was made possible by a grant from the Horace H. Rackham Trust Fund.

Induced Radioactivity in Strontium and Yttrium; Nuclear Isomers in Strontium

DAVID W. STEWART*

Departments of Chemistry and Physics, University of Michigan, Ann Arbor, Michigan

(Received August 16, 1939)

In revising and extending previous work on induced radioactivity in strontium and yttrium, it was found that with stronger activation by deuterons and neutrons, more accurate determinations could be made of the radioactive decay periods, and measurements of beta- and gamma-ray energies could be made with greater certainty. Periods of 2.0 ± 0.2 hours, 14 ± 2 hours, and 82 ± 4 hours were found in yttrium separated from strontium bombarded with 7-Mev deuterons. The first of these periods was assigned to Y^{88} , and the other two either to Y^{88} and Y^{87} , or to isomeric forms of either of these. Periods of 3.0 ± 0.1 hours and 55 ± 5 days, produced in strontium by bombardment of that element with deuterons and neutrons, were

assigned to the decay of isomeric forms of Sr^{89} , and the nature of that isomerism was investigated. From measurements in the cloud chamber, the maximum energy of the beta-rays from the 3-hour isomer was found to be 0.60 Mev, those from the 55-day isomer had an upper limit of 1.50 Mev, and the gamma-radiation which accompanied the 3-hour decay was found to have two components, of 0.55 Mev and 1.10 Mev. A tentative energy level diagram suggests that the metastable state of Sr^{89} decays first by the emission of a beta-particle and then by the emission of either one or two gamma-rays. The ground state of Sr^{89} decays directly to the ground state of Y^{89} without the emission of gamma-radiation.

INTRODUCTION

IN a previous paper,¹ radioactivity induced in strontium and yttrium by bombardment with deuterons and both fast and slow neutrons was reported. Radioactive isotopes with half-life periods of 3.0 ± 0.1 hours and 55 ± 5 days, both emitting negative electrons, were found in strontium and were identified with the decay of isomeric forms of Sr^{89} . Periods of 2.0 ± 0.1 hours, positive active, and 60.5 ± 2 hours, negative active, were found in yttrium and were assigned to Y^{88} and Y^{90} , respectively. The beta-ray spectra associated with the four periods were also measured in a 6-inch hydrogen-filled cloud chamber in a magnetic field.

Recently, improvements in the cyclotron have made available more intense beams of deuterons, and hence greater neutron intensities, and it has been possible to extend and revise the work previously reported.

EXPERIMENTAL PART

Arrangements for bombarding targets of strontium and yttrium nitrates, and for separating chemically the resulting activities were the same as reported previously.¹ Deuterons were accelerated in the cyclotron and were available at

energies between 6 and 7 Mev, in currents of from 10 to 20 microamperes. Material was exposed to slow neutrons inside paraffin blocks at a distance of about 30 cm from the beryllium target on which the deuterons were allowed to fall.

Measurement of radioactive decay was made on a Lauritsen type electroscope, and on a Wulf string electrometer using an ionization chamber filled with Freon (difluorodichloromethane).

Measurement of beta-ray energies was done in a hydrogen-filled cloud chamber twelve inches in diameter, in a magnetic field uniform to 0.5 percent throughout the chamber. Samples were placed against the inner wall of the chamber and were covered only with thin Cellophane tape. Gamma-rays were measured by observing recoil electrons ejected from a carbon absorber placed diametrically across the chamber. The gamma-ray source was placed behind a lead collimator outside the chamber, in the manner described by Richardson,² who also was responsible for the design and construction of the apparatus used. The absorber was of paper, treated with paraffin and lampblack, and having a density of 0.037 g/cm^2 . Only those recoil tracks were measured which had an initial direction within $\pm 10^\circ$ of the forward direction of the gamma-ray.

Stable isotopes of strontium and yttrium and neighboring elements are shown in Fig. 1, where figures refer to percent abundance of the isotopes.

* Present address, Department of Chemistry, Columbia University, New York.

¹ D. W. Stewart, J. L. Lawson and J. M. Cork, *Phys. Rev.* **52**, 901-6 (1937).

² J. R. Richardson, *Phys. Rev.* **55**, 609-14 (1939).

AT. WT.	84	85	86	87	88	89	90	91	92	93	94	95	96
Rb 85		(72.7)		(27.3)									
Sr 88	(0.5)		(9.6)	(7.5)	(82.4)								
Y 89					(100)								
Zr 90							(4.8)	(11.5)	(2.2)		(17)		(1.5)

FIG. 1. Stable isotopes with their relative abundance.

RADIOACTIVE ISOTOPES OF YTTRIUM

When pure strontium nitrate was bombarded with deuterons and yttrium separated from the products, a decay such as is shown in Fig. 2 was observed. By analysis, three periods, of 2.0 ± 0.2 hours, 14 ± 2 hours, and 82 ± 4 hours, were identified in a number of duplicate experiments. The shortest period was observed in the cloud chamber to emit positrons, as previously reported, and the two longer periods were found to emit negative electrons. These results indicate that the longer period activity previously obtained in yttrium can no longer be identified with the 60.5-hour period of Y^{90} , and hence there is no further reason to postulate a $Sr^{88}(H^2, \gamma)Y^{90}$ reaction, as suggested in the preliminary report.

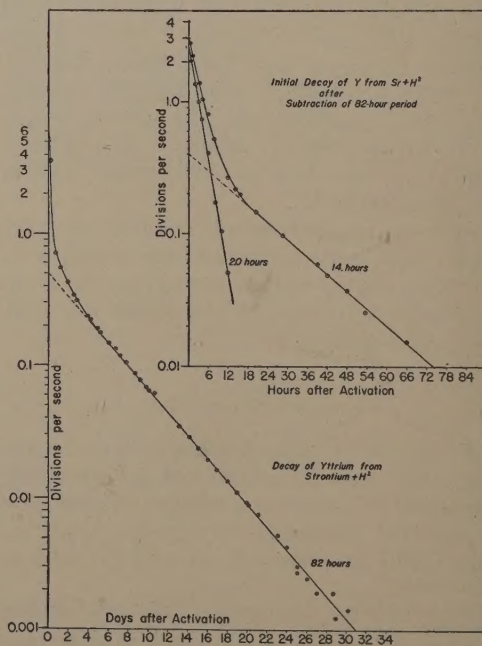
The possibility that the 14-hour period might be due to Na^{24} , from a contamination of sodium in the original material, was carefully investigated. The original strontium nitrate was recrystallized four times, twice from nitric acid and twice from water, with centrifuging of the crystals each time. In addition, in other experiments, sodium chloride was added in excess to the sample after bombardment and the usual chemical separation of the radioactive yttrium made from both the strontium and sodium present. In all cases, the three activities remained with the yttrium isotopes.

Since only the 2-hour period was obtained by bombarding yttrium with fast neutrons, the 14- and 82-hour periods cannot definitely be assigned to particular isotopes of yttrium. It is most likely that they are due to Y^{85} and Y^{87} , formed from Sr^{84} and Sr^{86} by (H^2, n^1) reactions, or to isomeric forms of either of these yttrium isotopes. The much greater abundance of Sr^{86} , as a starting material, would suggest Y^{87} as the probable product. The observed negative decay of such an isotope requires the existence of at least one unknown stable isotope of zirconium, or a K -electron capture process, in which the observed

beta-particles are actually due to the internal conversion of a gamma-ray following such capture. Present mass-spectrograph data for zirconium show no stable isotopes lighter than Zr^{90} , but it is possible that other, lighter, isotopes may still be found. The radiations from the longer periods were not intense enough at best to be examined conveniently for evidences of K -electron capture, nor were the beta-spectra measured to identify internal conversion electrons.

NUCLEAR ISOMERS IN STRONTIUM

The preliminary identification of the 3-hour and 55-day periods in strontium, produced both by deuterons and neutrons, as due to the decay of isomeric forms of Sr^{89} has been further confirmed. The production of the 3-hour isomer is much favored over the one of 55-day half-life when neutrons are used instead of deuterons, and it has been possible to prepare relatively strong sources of the 3-hour activity almost free from the longer period isomer. These have been used for cloud chamber studies of the beta- and gamma-radiation which accompanies this decay. The 55-day isomer, produced most strongly by

FIG. 2. Decay of yttrium from $Sr+H^2$.

deuteron bombardment of strontium, has no gamma-radiation. The upper limits of the two beta-spectra have also been redetermined more accurately. The observed maximum energy for the beta-rays from the 3-hour isomer was found to be 0.60 Mev (Konopinski-Uhlenbeck extrapolation=0.65 Mev), from a distribution of 794 tracks as shown in Fig. 3. The observed upper limit for the 55-day isomer is 1.50 Mev (K-U extrapolation=1.82 Mev), as determined

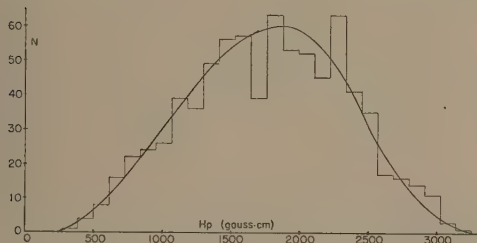


FIG. 3. Beta-rays from Sr^{89} (3-hour). 794 tracks; $H=222$ gauss; Observed upper limit = 0.6 Mev.

from 551 tracks shown in Fig. 4. These values are in good agreement with the independently determined values reported previously.¹

The energy of the gamma-rays emitted during the decay of the 3-hour isomer was determined from a distribution of 475 recoil tracks in the cloud chamber. Even with the strongest sources available, the loss of intensity in the collimation process was so great that more than 3000 photographs were required to give this number of measurable recoils, all meeting the requirement as to direction previously described. The distribution of tracks with energy is shown in Fig. 5. From this, at least two components in the gamma-radiation can be identified. The first, corresponding to a maximum recoil momentum given by the point *A*, has an energy of 0.55 Mev; the second, limited by the point *B*, corresponds to a gamma-ray of 1.10 Mev. After correcting for the greater probability of recoil ejection by the gamma-ray of lower energy, an intensity ratio of 5 : 1 between the lower and higher energy lines is probably of the correct order of magnitude.

Since it has been shown that the beta-spectra of the two isomers are quite different, and also because the gamma-rays are associated with the

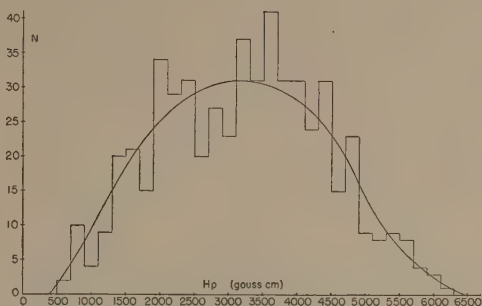


FIG. 4. Beta-rays from Sr^{89} (55-day). 551 tracks; $H=401.4$ gauss; Observed upper limit = 1.50 Mev.

period of shorter half-life, it must be concluded that the isomers are of the second type described by Bethe.³ In this type of decay, the isomer corresponding to the metastable state emits a beta-particle directly, following this with the emission of one or more gamma-rays, possibly in a cascade process. If the ground and metastable states of the radioactive nucleus are to be separated by only a small energy difference, the sum of the beta- and gamma-ray energies for the one isomer must be approximately equal to the beta-ray energy of the other isomer. Applying this requirement to the experimental data, an energy level diagram for Sr^{89} and its decay product, Y^{89} , is obtained such as that shown in

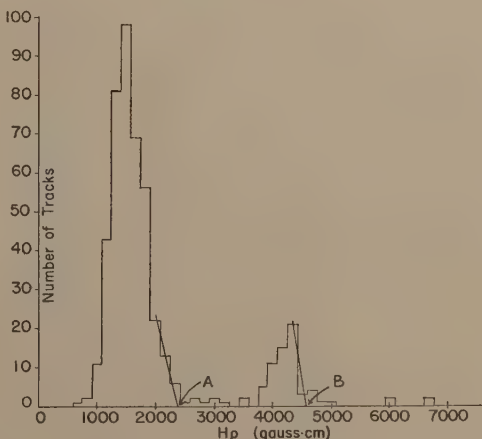


FIG. 5. Recoil electrons from gamma-rays of Sr^{89} (3-hour). Carbon radiator—475 tracks.

³ H. A. Bethe, Rev. Mod. Phys. 9, 226 (1937).

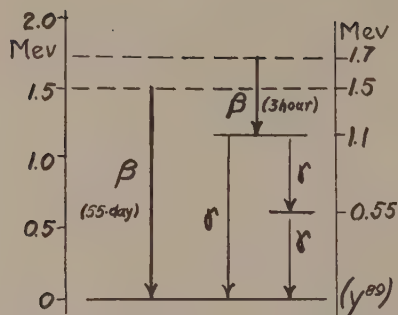


FIG. 6. Suggested energy levels in Sr^{90} .

Fig. 6. Observed values of the upper limits of the beta-spectra are used throughout. Dotted lines indicate possible levels in the radioactive nucleus, and solid lines those in the product.

In this scheme, the separation of the ground and metastable states is found to be 0.2 Mev, and the gamma-decay is assumed to take place in either of two alternative processes. In one, the total energy is dissipated in one gamma-ray

of 1.1 Mev; in the other process, two gamma-rays of approximately the same energy (and therefore not resolved in the distribution shown in Fig. 5) are emitted in succession, each of about 0.55 Mev. The larger number of low energy quanta observed suggests that the cascade process is slightly more probable than the emission of the energy in one step. A larger number of tracks would be required to fix more definitely the ratio between the two processes.

ACKNOWLEDGMENTS

The author is indebted to Professor K. Fajans of the Department of Chemistry for his helpful interest and guidance throughout the work reported here. Particular thanks are due to Professors J. M. Cork and H. R. Crane, and to Drs. B. R. Curtis, J. L. Lawson, and Gerald Tape, all of the Department of Physics, for their cooperation. This investigation was made possible by grants from the Horace H. Rackham Trust Fund.

